Evaluation of Nitride Layer on Ti-6Al-4V Titanium Alloy by Tungsten Inert Gas (TIG) Nitriding Method

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Evaluation of Nitride Layer on Ti-6Al-4V Titanium Alloy by Tungsten Inert Gas (TIG) Nitriding Method

Thesis submitted in partial fulfillment

of the requirements of the degree of

Master of Technology

in

Mechanical Engineering

by

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based on research carried out

under the supervision of

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May, 2016

Department of Mechanical Engineering

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CERTIFICATE

This is to certify that the thesis entitled "**Evaluation of Nitride Layer on Ti-6Al-4V Titanium Alloy by Tungsten Inert Gas (TIG) Nitriding Method**" being submitted by **Chirag Panwariya (214ME2343)** for the partial fulfillment of the requirements of **Master of Technology degree** in **Production Engineering** is a bonafide thesis work done by him under my supervision during the academic year 2015-2016 in the Department of Mechanical Engineering, National Institute of Technology Rourkela, India.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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Declaration of Originality

I, Chirag Panwariya, Roll Number 214ME2343 hereby declare that this dissertation entitled *Evaluation of Nitride Layer on Ti-6Al-4V Titanium Alloy by Tungsten Inert Gas (TIG) Nitriding Method* presents my original work carried out as a postgraduate student of NIT Rourkela and, to the best of my knowledge, contains no material previously published or written by another person, nor any material presented by me for the award of any degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this thesis have been duly acknowledged under the sections "Reference". I have also submitted my original research records to the scrutiny committee for evaluation of my thesis.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present thesis.

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Acknowledgment

I wish to express my sincere gratitude to my supervisor Dr. M. Masanta, for giving me an opportunity to work on this project, for his guidance, encouragement and support throughout this work and my studies here at NIT Rourkela. His impressive knowledge, technical skills and human qualities have been a source of inspiration and a model for me to follow.

I express my sincere gratefulness to Dr. S. S. Mohapatra, Head of the Department, Mechanical Engineering, NIT Rourkela for giving me an opportunity to work on this project and allowing me the access to valuable facilities in the department.

I would like to mention the help and support received from Mr. Arabinda Khuntia, technical staff Production Lab. And Mr. S. Tigga workshop assistant. The assistance and support received from all the members who contributed and who were part of this project, whose names could have not been mentioned here, are highly acknowledged.

I am also thankful to Mr. Chinmaya Sahoo, Mr. Tijo D. and Mr. Kamlesh kumar PhD research scholars and my friends for extending their technical and personal support and making my stay pleasant and enjoyable.

It’s my wish to express my gratitude towards my late grandfather and I thank my parents and family for their eternal effort.

May 24, 2016 *Chirag Panwariya*
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Abstract

In order to improve the micro-hardness and wear resistance, nitride layer has been formed on Ti-6Al-4V alloy by using trailing nitrogen gas by TIG (Tungsten inert gas) melting process. Effect of nitrogen gas flow on the formation of nitride layer and its mechanical properties like micro-hardness and wear resistance have been investigated. Depending on the energy density and the amount of nitrogen gas, Titanium nitrides, Titanium-Aluminium-Nitride and their intermetallic compound are formed on Ti-6Al-4V alloy, which resulted in improvement the surface hardness and wear resistance of Ti-6Al-4V alloy. Vicker's micro-hardness tester was used to measure the micro-hardness at the cross section of the nitride zone. Hardness of nitride zone is found two to three times higher than the hardness of titanium alloy. Wear test results revealed that the wear resistance of Titanium nitride layer is up to ten times more than the Ti–6Al–4V substrate. Also effect of TIG welding current and scan velocity on the nitrided layer and corresponding microstructure has been investigated.

***Keywords*: TIG Melting; Hardness; Wear resistance; XRD analysis; Microstructure**.

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Chapter 1

Introduction

In present era, surface of machine tool components is always subjected to wear, corrosion, fatigue and creep, in certain condition. If suitable surface modification techniques in not applied these factor increases by time. Surface treatment is essential for modern machine tool components in aerospace, automobile and nuclear industry. Material for industrial application is selected on the basis of two different point of view. First one is for core material having bulk properties likewise high molecular density, high strength, low weight, high modulus of elasticity and hot hardness, while the second one is surface should have good belongings like as high wear and corrosion resistance, high resistance against fertting damages. However, it is unlikely to most material that has all these surface properties.

Surface properties can be improved by using different surface treatment techniques to provide hard protective layer against damages [Podgornik et al., 2001]. Surface nitriding can be used to produce a hard and protective layer to improve surface hardenability, wear resistance and fatigue strength of metals and its alloy [Mridha et al., 2005]. For last few decades, TiAlN and TiN coatings have been applied to tools, dies, and many mechanical parts due to their excellent properties especially at high temperature, low density, high hardness, good electrical and thermal conductivity, high melting point, and high corrosion resistance [Munz et al., 1986; Seog et al., 2002].

The purpose of this research is to produce the hard protective layer on Ti-6Al-4V alloy by the implication of TIG welding torch in the nitrogen environment. Reaction of nitrogen with melted titanium alloy produces TiN and some other hard intermetallic those are responsible for surface improvement of Ti-alloy.

1.1 Different surface treatment techniques used for surface modification

Surface treatment is the advancement in the field of engineering for enrichment of mechanical properties like as wear resistance, hardness and corrosion resistance of work material [Tian et al., 2006; Muthukumaran et al., 2011; Borgioli et al., 2005]. Techniques for the modification of surfaces are evolving rapidly. There are three general techniques used to modify surfaces: add material, remove material, and change the material already present. Several new processes making thin film coatings (sub-micron) have come from the electronics and optics industries like as Physical Vapour Deposition, Chemical Vapour Deposition, Plasma cladding, Laser cladding, Thermal spraying, and TIG cladding [Funatani, 2000; Yu et al., 2009; Shamanian et al., 2010]. In case of Vapour deposition techniques, the coating material in vapour form condenses onto a surface and after solidification provide a protective layer. Surface properties can be changed without addition or removal of material by use of laser and electron beam thermal treatments. Ion implantation can be used to add material to surfaces, modify surface, and change microstructures. In most of the surface treatment technique, high energy density is used to melt the metal which provides steep temperature gradient, which leads to rapid solidification and higher melted depth is obtained. Surface treatment by using electron beam processing and LASER heat treatment gives best result but that are very expensive process. Heat treatment by using GTAW welding setup gives a qualitative result with low cost so the TIG welding method is the suitable replacement for surface melting techniques [Jeshvaghani et al., 2011; Lin et al., 2003; Sarker et al., 2010; Mridha 2005].

Gas Tungsten Arc Welding (GTAW) commonly known as Tungsten inert gas welding can also be used to modify the surface properties and microstructure. While during surface modification in nitrogen environment TIG welding treated as Tungsten inert gas nitriding which will be discussed later in details.

Different methodologies to acquire surface hardening are discussed in short:

Diffusion Process: This process leads to the modification of the surface configuration by introducing carbon, boron and nitrogen etc. on the surface.

Carburizing: In this process specimen along with carbonaceous material such as charcoal, is packed in a container and kept in a furnace. The pack is heated to a temperature between 800-950 ^{0}C and held for a period of 4 to 20 hours on heating to provide a hardened layer.

Nitriding: Alloying elements such as aluminium, chromium, vanadium, tungsten and molybdenum have very high tendency to form hard nitrides when they come in contact with nitrogen. Hardening of the Titanium alloy is achieved by introducing nitrogen or TiN powder in preplaced method.

Boronizing: Boronizing is also known as Boriding. It involves the creation of boron compound onto the surface by diffusion of boron atoms into the base metal in a thermochemical way. The temperature lies in the range of 700 °C to 1000 °C. Boronizing is suitable for non-ferrous and ferrous metal and ceramics also. Boriding increases abrasion resistance and coefficient of friction.

Maximum obtainable hardness by boriding are lies in the range of 750-1600 HV, and Maximum obtainable Hardness value can be 2800 HV for boriding.

Flame hardening: In this an oxyacetylene flame is moved over the workpiece followed by quenching spray. The depth of layer being hardened is determined by the velocity of the flame and material properties. This process is carried out at 200 ^{0}C and most suitable for complex contour such as gear, engine crankshaft, cams etc.

Induction hardening: Induction hardening is the best-suited process in respect of non-affecting the core microstructure. Induction hardening is used to improve wear resistance, increasing hardness, and fatigue life. Heating is carried out by placing the specimen in a high-frequency magnetic field. The depth of penetration decreases as the frequency increases.

LASER heat treatment: Laser heat treatment increases wear resistance and increases the fatigue strength due to the compressive stresses induced on the workpiece surface.

Process is carried out with a well-defined beam of intense laser light source, used to heat treatment of specimen. The intense energy created by LASER heat source is transferred to the material surface, which is responsible for creating a hardened layer on the surface by metallurgical transformation.

1.2 Tungsten Inert Gas welding setup

TIG or Gas tungsten arc welding process is an inert gas shielded arc welding process using non-consumable electrode. Shielding gas used in welding either argon or helium or the combination of both in some cases. The electrode generally used are pure tungsten or thoriated tungsten. The zirconia added tungsten electrode is also used, which is better than pure tungsten electrode but inferior to thoriated tungsten electrodes.

The TIG welding setup consists of a welding torch at the centre of which tungsten electrode is fixed as shown in Figure 1. The inert gas is supplied to melted zone through the annular path surrounding the tungsten electrode to effectively insulate the weld pool from the atmosphere.

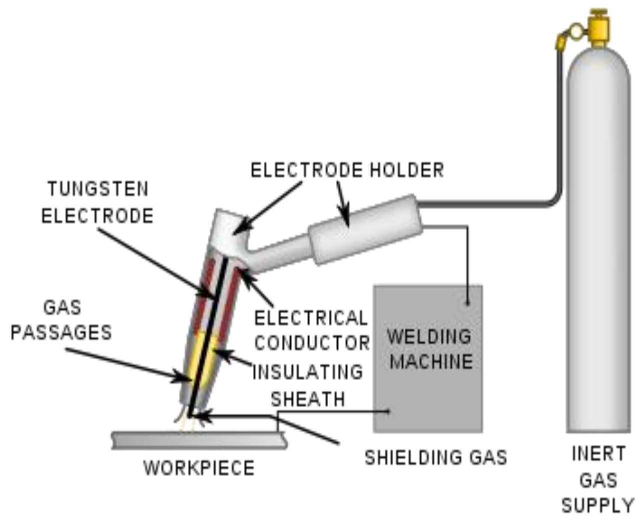


Figure 1- Schematic representation of TIG welding setup.

1.3 Tungsten inert gas nitriding

Tungsten inert gas melting setup is one of the most versatile techniques of surface alloying and surface treatment [Lin et al., 2005]. Tungsten inert gas melting assisted by nitrogen gas is used to produce nitride layer on the substrate surface [Sarker et al., 2010; Sarker et al., 2011; Mridha et at., 2005]. Heat treated area by TIG welding heat source is covered by nitrogen gas with the aim of producing nitrides. Argon is used as a shielding gas to protect the surface from contamination and to avoid oxide formation. Nitrogen gas is provided with the aim of transforming titanium alloy into titanium nitrides. GTAW provides high energy density due to which rapidly rise in temperature, and melted titanium alloy react with the supplied nitrogen gas resulted in the formation of Titanium nitride. Further high flow of nitrogen gas causes sudden cooling of the substrate and quenching of melted zone.

The formation of titanium nitrides and their intermetallic compound on the surface of titanium or Ti- alloy substrate and quenching effect modify the surface properties. As a result surface hardness of the material increases, and improves the wear resistance and surface microstructure. It produces high quality nitride layer at low cost for a wide range of materials. By proper controlling the parameters a thick hardened surface (in range of few hundred microns) can be obtained by this process.

Cost of GTAW nitriding setup is less than the laser nitriding, plasma nitriding and other source of nitriding. Along with the cost of setup, maintenance and running cost of GTAW nitriding setup is also very less as compared to laser nitriding. Moreover, GTAW does not suffer from less absorption of laser beam by metallic surface and powder like laser nitriding.

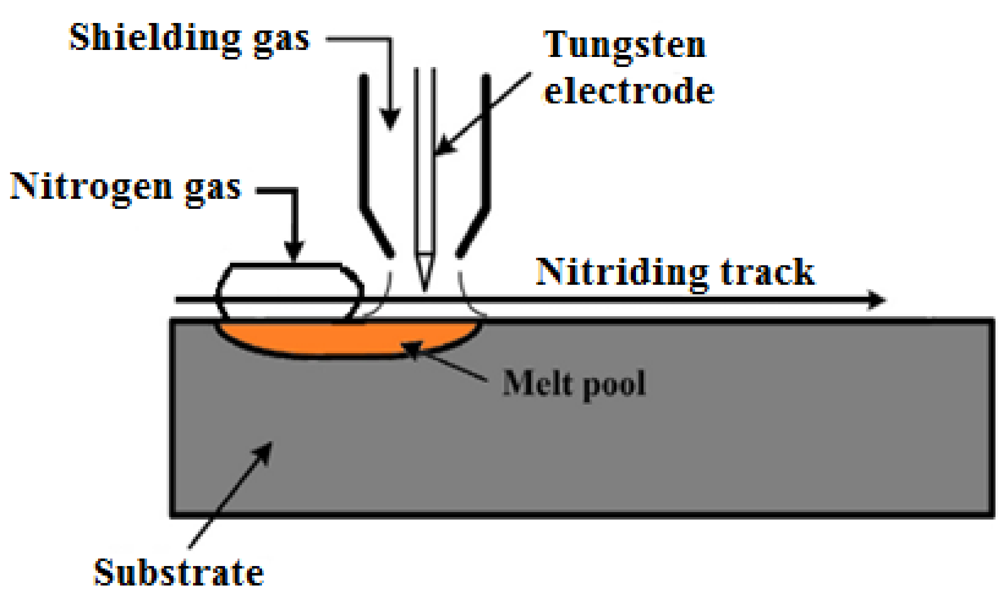


Figure 2 - Schematic representation of TIG surface nitriding.

1.4 Advantages of TIG nitriding

Tungsten inert gas (TIG) surface treatment process offers the several advantages, as follows:

- Large-scale availability
- Easily portable
- Low equipment cost
- Manual operation as well as automated operation is possible
- No vacuum is required which is basic need in Electron beam nitriding.

1.5 Limitation of TIG nitriding

Along with prominent advantages it has certain limitation such as:

- Slow as compared to other process such as laser nitriding or electron beam nitriding.
- Large heat affected zone is produces and sometimes surface deformation occurred if operating conditions are inappropriate.

1.6 Applications of TIG nitriding

TIG nitriding can effectively apply in the field of:

- Preventive protection of particular areas or whole workpiece to resist severe wear conditions (abrasion, corrosion etc.)
- Automobile and Aerospace industry.
- Crankshafts, die-casting, gears, cam followers.

Chapter 2

Literature review

Ti-6Al-4V alloy is the best suited material in the aerospace, automobile, chemical, biomedical, and nuclear industries because of prominent characteristics i.e. high strength, low density, and decent electrical and thermal conductivity, non-magnetic, good corrosion resistance. However Titanium alloy has poor wear resistance and high galling and fretting damages under severe loading condition. Different methods such as boriding, carbiding, and nitriding (as we discussed above) are available to improve the hardness wear resistance of this alloy. Among these methods nitriding is a best suited for Ti alloy due to reactivity of Ti with Nitrogen and formation TiN, Which is hard, wear resistance and having low coefficient of friction. In Nitriding of Ti alloy under the nitrogen environment produces hard and protective layer.

In the beginning, surface nitriding was performed with the help of LASER due to its specific advantages. It was started by [**Katayama et al., 1983].** Afterwards, there have been many researcher works on economical method of nitriding like TIG nitriding **[Razavi et al., 2007; Bell et al., 1990; Zimnicki et al., 1998].** In this section literature review on various laser nitriding as well as TIG nitriding of Ti and Ti- alloy have been discussed.

2.1. Different Research work on nitriding

2.1.1 LASER nitriding

Dahotre et al. [20] explores that the implication of LASER beam with the Nitrogen gas flow rate of 20 l/min at atmospheric pressure inside inert enclosure on Ti-6Al-4V form hard titanium nitrides. Amount of the nitrogen diffused on Ti alloy layer depends on several factors likewise LASER processing parameters (beam power, scan speed), thermal and physical properties of base material, mode and rate of heat transfer and flow of molten material.

Experiment shows that, the depth of nitrogen diffusion increases with the increase in LASER energy density, laser interaction time and decreasing scanning speed. Higher the amount of the nitrogen diffused, higher hardness was achieved along with high wear resistance.

Nwobu et al. [21] studied the laser nitriding of commercial purity (CP) Ti and gamma TiAl based alloy under Ar–N_2 gas mixtures. It was observed that TiN dendrites were formed in CP Ti, while TiN and intermetallic compound Ti_2AlN form in the gamma Ti alloy. Maximum surface hardness was achieved for CP Ti alloy lie in the range of 1200-2000 HV and for gamma Ti alloy was 1350 HV.

Yilbas et al. [22] compared the laser assisted nitriding with the help of CO_2 laser and the TiN coating by the physical vapour deposition method. Results showed that, the thickness of the clad layer obtained was 80 µm by LASER assisted nitriding. The nitrided zone was free from cracks and other irregularities such as porosity and voids. On the other hand a uniform layer of 2 µm TiN coating was obtained by PVD method.

Abboud et al. [23] investigated the effect of high power source of CO_2 LASER on Ti-6Al-4V substarte with the aim of high hardness and high wear and erosion resistance. Effect of different processing parameters of LASER source i.e. scanning speed, nitrogen dilution, focusing diameter on the microstructure, hardness and wear resistance of the nitride layer were studied. Hardness achieved was in the range of 500-800HV. Cracks were observed in the sample processed at slow scanning speed and high laser power. Dilution of nitrogen gas with argon produces crack free coating layer without pores that marginally reduces the hardness value.

Fu et al. [24] synthesized TiN reinforced Al metal matrix composite coating on Ti6Al4V alloy by simultaneous feeding of Al powder and nitrogen gas through nozzle during a laser nitriding process. Crack and pores free coating was observed with laser beam of power range from 1.8 KW to 3.0 KW. Maximum hardness of the coating surface was achieved upto 1600 HV. It was observed that, the micro hardness was decreased gradually with increasing distance from the coating surface.

Balla et al. [25] fabricate TiN coating on Ti-6Al-4V alloy by Laser engineered net shaping technology for improving wear resistance and surface hardness. Maximum hardness of the coated layer was increased upto 1138 HV. Wear resistance of the composite coating was increased from 3.76×10^{-6} to 2.8×10^{-4}.

Mridha et al. [26] compared the effect of laser nitriding of Ti-6Al-4V alloy in weak and strong nitrogen environment. Authors observed cracks on the nitride surface under pure nitrogen environment that can be reduced by decrease in nitrogen gas flow rate. Authors also observed that laser nitriding in diluted nitrogen environment completely eliminate the crack forming tendency. Maximum hardness achieved under pure nitrogen and diluted nitrogen environment was 13 and 6 times of the surface hardness of Ti6Al4V alloy respectively.

Kamat et al. [27] examined the effect of high power source of CO_2 LASER on Ti-6Al-4V alloy by creating nitrogen plasma in air. Microstructures formed by laser sustained plasma nitriding are function of stand-off-distance, nitrogen to argon gas flow ratio, scan speed of CO_2 laser. Higher nitrogen to argon gas ratio was responsible for higher nitride forming capability but it also increases crack forming tendency. While dilution of nitrogen gas by argon decreases crack formation, surface roughness and surface oxidation. TiN dendrites on **Ti64** alloy increases by decreasing scan speed of laser, TiN dendrites also increases by increasing nitrogen to argon gas flow ratio.

Ng et al. [28] fabricate the TiN grid network on Nickel-Titanium alloy by laser gas nitriding method to improve the wear resistance of Ti alloy. Laser parameter was selected in such a way that smooth surface finish was obtained. Depending upon the energy density of laser beam and amount of Nitrogen gas diffused in atmosphere finer grid structure of titanium nitride was formed. Wear factor decreases 35 to 55 % on nitride layer of NiTi alloy.

Yongqing et al. [29] endeavoured to improve surface properties of pure titanium by ND-YAG laser assisted nitriding. Before nitriding, a layer of nickel and chromium powder of 70 to 30% ratio was provided to prevent the crack and pores formation. Nitrogen gas in form of jet is supplied in melted zone to form titanium nitrides. Titanium easily reacts with nitrogen because of having strong affinity of titanium towards nitrogen. Maximum hardness achieved was upto 1600 HV.

2.1.2 TIG nitriding

Dyuti et al. [30] attempted to form a Clad layer of 1 mm thickness can be formed by melting Ti and Al powder mixture preplaced on a plain carbon steel, with the application of TIG welding torch of energy density ranging from 540-675 J/mm in the nitrogen environment. Ti-Al nitrides and Ti-Al intermetallic were formed due to heat intensity of TIG torch and dispersed irregularly throughout the melt pool. Hardness of the cladd zone depends upon the concentration of the dendrites, which is higher at near the surface area as compared to the shallower melt depth. Maximum surface hardness was achieved around 900 HV that is nearly 4.5 times then the base material hardness (180 HV). It was observed that, the microstructure of coating was changing from finer at the surface to the coarse dendrites at the bottom.

Mridha [31] investigated the use of TIG arc heat source on the commercial purity titanium in inert nitrogen environment to produce TiN layer on the melt surface. It was observed that, Maximum hardness on the modified layer depends on the energy density and concentration of the nitrogen gas. The experimental results revealed that by reaction of N_2 gas with Ti substrate porous edges were manifest on both sides of the nitrided track mainly due to the evolution of the excess nitrogen gas during cooling.
Intruding TIG torch of energy density in the range of 46 MJ/m^2 to 182 MJ/m^2 produced melt layer upto 1 mm thickness. Resolidified melt pool produced a hemispherical nitrided track with dendritic microstructure of TiN. Higher hardness value upto 2000 HV was achieved for nitrided CP-Ti.

Sarker et al. [32] synthesized titanium-aluminium dispersed hard titanium layer in the nitrogen environment. Thickness of Ti-Al-N coated layer upto 1 mm on mild steel was observed with the help of TIG welding heat source of energy density 540, 608, and 675 J/mm. Maximum hardness was achieved for hard Ti-Al nitrides and Ti-Al intermetallic compound upto 900 HV and it was found that hardness value is higher on the surface and decreases towards the depth.

Lin et al. [33] deposited titanium nitride powder onto Ti-6Al-4V substrate to increase the wear resistance and hardness by employing GTAW arc scanning using argon as shielding gas. Hardness of the deposited layer was observed twice of the base material hardness. While the wear resistance of the clad layer was found ten times higher than the base material. Voltage and current used in GTAW torch was 17 V and 120 A (DC) respectively, with a welding torch of scanning speed 0.65×10^{-3} m/s.

Hojjatzadeh et al. [34] performed the surface alloying of AISI 1045 steel substrate with a preplaced layer of ferrotitanium powder under different ratio shielding gas mixture of nitrogen and argon. It was found that the microstructure of the clad layer obtained after treating the substrate consisting ferrite, Fe_3C and TiN dendrites that improved micro hardness of the substrate upto 472 HV. Analysis of experiments indicates that pores were formed on the outer layer of cladding with 70-100% of nitrogen and by decreasing the amount of nitrogen gas pores were eliminated. On the other hand increasing the amount of nitrogen gives the higher melt depth and resulting higher hardness. It was found that by reducing the nitrogen content in the shielding gas the microstructure of the layers became comprised of $Ti(C_xN_y)$ that distributed in a matrix phase.

Lin et al. [35] performed nitriding on Ti-6Al-4V using Nitrogen as a shielding gas by using TIG welding system. In this work authors found that, by using different nitriding source, different phases can be formed. TiN powder as a nitrogen source gives dual phase of TiN and TiN_x, while Nitrogen gas as a nitrogen source produce only TiN. Maximum hardness upto 1810 HV was obtained by using Nitrogen gas. They have also observed that average size of the TiN dendrites was affected by the heat input, for high heat input (in addition of deeper nitriding depth) dendrite microstructure was achieved.

Sohi et al. [36] studied the effect of nitrogen to argon ratio in shielding gas on AA5052 Aluminium by using gas tungsten arc melting torch. He observed the phases of Aluminium nitrides on the nitride sample by the help of XRD analysis. Maximum surface hardness of Aluminium was increased from 52 HV to 1411 HV i.e 25 times of the base hardness of AA5252 aluminium.

Nemani et al. [37] perform the liquid phase TIG surface nitriding on Ti-6Al-4V alloy by preplacing Chromium powder on Ti alloy, carried out at two distinct level of heat density. Nitrogen gas is diffused in atmosphere with aim of forming Nitrides of chromium and titanium. Maximum surface hardness achieved of nitride layer was 1200 HV as compared to 280 HV base hardness of substrate. Weight loss of nitride layer was 7 times lower than that of untreated Ti-6Al-4V alloy.

2.2 Motivation and objective

From the literature it is revealed that surface modification of Ti and Ti alloy has been done by several researchers by using LASER beam coating, Electron beam coating, Thermal spraying, Ion Implementation, Plasma spraying and Tungsten inert gas cladding [Podgomik et al., 2001; Munz et al., 1986; Funatani 2000; Yu et al., 2009]. Lot of works have been also done in the field of carburising for improving the surface properties of Ti alloy by producing hard TiC phase. However nitriding of Ti and its alloy gives better performance when high hardness along with low coefficient of friction is required. Further for maintaining the bio-compatibility of Ti alloy nitriding is more useful.

Although LASER assisted nitriding is an emerging method, however its high capital cost and technical complexity restrict the process in small scale industry.

Thus TIG nitriding, an alternative method has been selected for the present work, where using a normal TIG welding setup nitriding of Ti-6Al-4V alloy has been performed.

On the basis of available literature, for the present work following objective has been made:

Formation of TiN layer on the Ti-6Al-4V alloy by trailing Nitrogen gas.

1. Measurement of Hardness Value of nitride layer both at surface and cross section.
2. Measurement of wear rate against tungsten carbide cobalt (WC-Co) ball by dry sliding wear test.
3. Study the effect of process parameter like as Current, scan velocity and Nitrogen gas pressure on Hardness and wear resistance of the modified layer.
4. Study the microstructure of the nitride layer and effect of TIG processing parameters on its microstructure.
5. XRD Analysis of nitride layer to identify different compound present in the modified zone.

Chapter 3

Experimental Planning and Procedure

3.1 Experimental planning

For present work, Ti-6Al-4V has been selected as a substrate for TIG nitriding process.Figure 3 demonstrate the flow of experimental planning and procedure of the present research work.

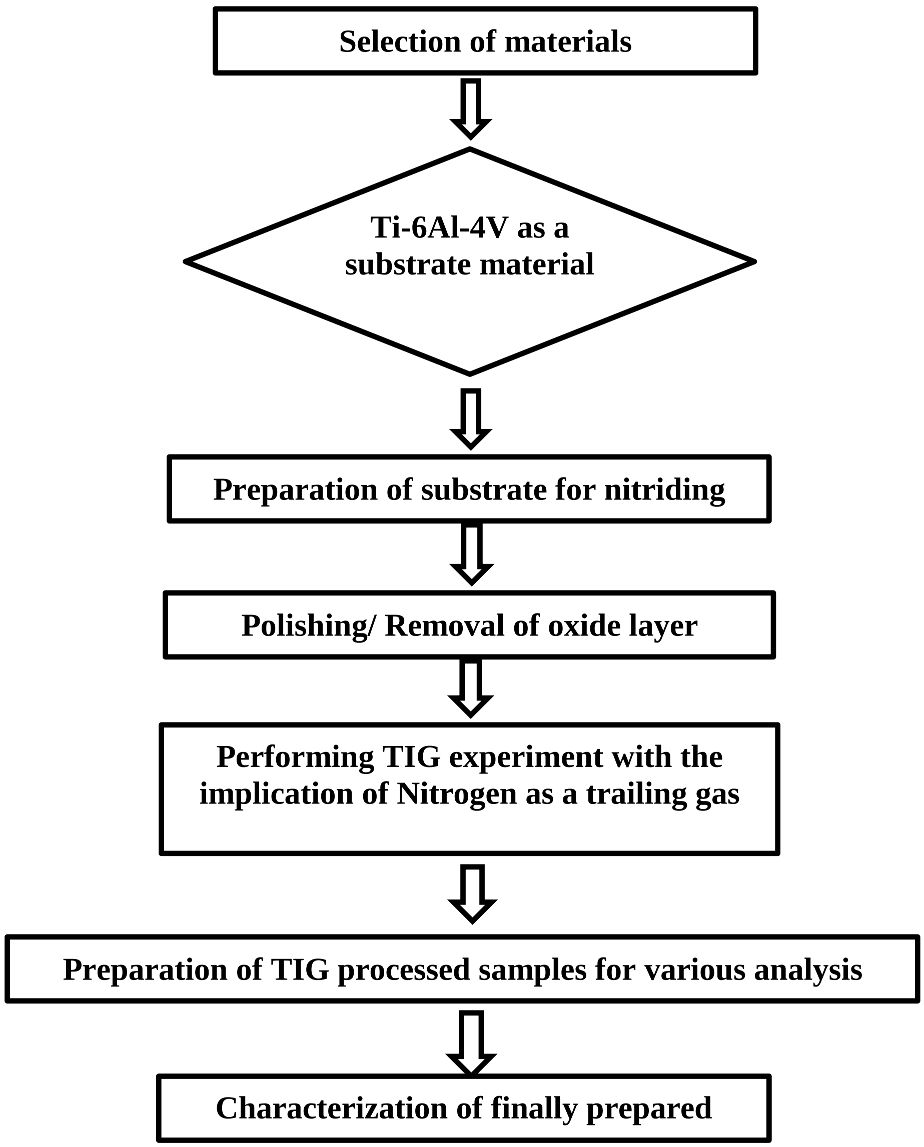


Figure 3 - Flowchart showing the experimental steps

3.2 Material selection

3.2.1 Substrate

Ti-6Al-4V a Titanium alloy (grade 5) of dimension 100 mm × 25 mm × 3 mm was used as substrate for present experiment. The typical physical and mechanical properties of Ti-6Al-4V alloy are shown in table 1.

Table 1 : Typical Physical and Mechanical Properties of Ti-6Al-4V alloy

Property	Value
Density	4.43 g/cm^3
Melting Point	1604-1660°C
Modulus of Elasticity	113.8 GPa
Thermal Conductivity	6.7 W/m.K
Electrical Resistivity	0.000178 ohm-cm
Thermal Expansion	8.9x10^{-6} /K
Tensile strength (MPa)	880
Compression Strength (MPa)	970
Hardness Vickers (HV)	334

3.3 Experimental setup used for nitriding

Nitriding of Titanium alloy is prepared with the aid of a semi-automated Direct current electrode negative (DCEN) polarity, TIG welding setup (FRONIUS TP-2200), which consist of the following parts:

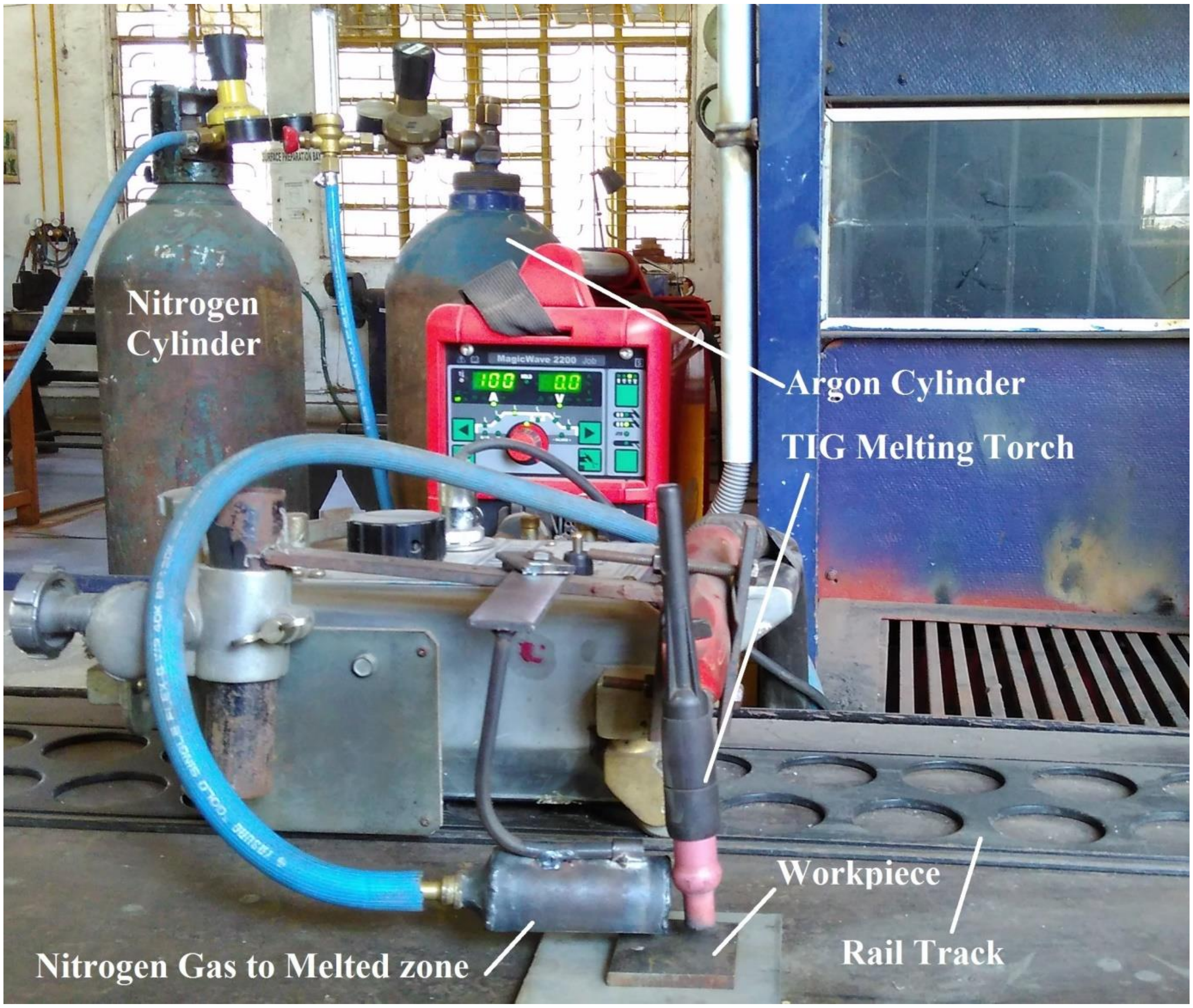


Figure 4 - TIG nitriding Setup

Rectifier: A Rectifier is used with the aim of converting alternating current into direct current having current range of 10-220 A. Current is a process parameter in the input form, and voltage comes out in the output form whose value depends upon the Arc gap for present experiments.

Speed control unit: It installed on TIG setup for precisely control the scan speed of welding torch. Torch is attached with the speed control unit whose scan speed can be regulated with the help of regulator.

Rail track: Movable tractor runs over this rail track in a particular speed.

TIG welding torch: The thoriated tungsten electrodes of diameter 2.4 mm was used which carry high currents and are most suitable which can strike and maintain a stable arc with relative ease.

Inert Gas supply: Shielding gas used in the melted zone is either argon or helium or the combination of both in some cases, to create an inert atmosphere aiming towards a stable arc. Nitrogen gas is used as a nitriding material for the purpose of forming hard protective layer of Titanium Nitrides and their intermetallic compounds.
Value of trailing nitrogen gas pressure used is 1, 1.5 and 2 bar having flow rate of 10-15 l/min.

3.4 Equipment used for the characteristics of TIG-Nitrided sample

Micro-hardness testing machine

Micro-hardness testing is performed by the help of Vicker Micro-hardness testing Machine on a microscopic scale. A highly precision diamond type indenter is used for impression onto the nitrided specimen both at the top surface and Cross section of the nitride zone at loads 50 gram. Both Diagonal lengths of the rombus are measured by using microscope. This gives the Micro-Hardness number of material in terms of (HV) value by standard formula.

Scanning electron microscope

Structure of the nitride sample had been studied at mico level by Scanning electron microscope (JEOL JSM-6084LV). The micrographs have been taken in the BEI (Back Scattered Electron Imaging) mode. The scanning electron microscope (SEM) is a diagnostic tool used to examine the microstructure of the exterior surface of the samples. High resolution images of the nitrided section had obtained from the nitrided sample.

X-Ray diffraction

Non-destructive X-ray diffraction testing is performed for obtaining different phases existing in the nitride layer on Titanium alloy by X'Pert (Model- ULTIMA-IV, made by RIGAKU Japan) X-ray Diffractometer. The scanning range was 20^o to 90^o. XRD is usually employed for phase identification and quantifiable analysis.

Wear testing Machine

Wear testing is a laboratory method for calculating the wear of specimen during sliding motion of nitrided sample fixed on rotating disk by using a pin-on-disk apparatus. Wear testing is performed under non-abrasive conditions. The primary areas of experiment are to measure the wear and coefficient of friction. Ball on disk type rotating wear machine under dry condition is used to measure the tribological properties of nitrided layer. Ball of tungsten carbide is fixed on the upper specimen and nitride sample rigidly fixed on disk on lower specimen is rotated. Ball was loaded and slid onto the rotating sample. During wear testing in dry condition wear testing machine is connected with the personal computer for data acquisition. Computer plotted the graph of coefficient of friction, frictional force and wear with respect to time individually.

Wear results are reported as volume loss in cubic millimeters for the specimen.

3.5 Experimental Procedure

3.5.1 Sample Preparation for Experiment

Before nitriding, specimen was polished by emery paper to ensure that no oxide layer were present and cleaned with the aid of suitable Acetone. GTAW (Gas Tungsten Arc Welding setup) heat source of direct current electrode negative polarity was used to melt the substrate. Argon is used as a shielding gas to protect the melted zone from atmosphere and Nitrogen as a source of formation of nitrides.

3.5.2 Process parameter for the experiment

Current (A), Nitrogen Pressure (bar), Scan Speed (mm/sec) is used as input parameter. Whose numerical value are given in table 2. Energy density at the melted zone can be calculated with the help of the given formula

$$Energy\ Density\ (J/mm) = \frac{Current\ (A) \times Voltage\ (V)}{Scanning\ Speed\ (mm/sec)}$$

Parameters used for TIG nitriding process are given in Table 2.

Table 2 : Experimental parameters of TIG-nitriding

Specimen	Current (Coaded)	Voltage (V)	Scan Speed (Coaded)	Nitrogen Gas Pressure (bar)
S 1	1	12.4	2	Without Nitrogen
S 2	1	13.8	1	1
S 3	1	12.5	1	1.5
S 4	1	13.6	1	2
S 5	1	13.5	2	1
S 6	1	12.4	2	1.5
S 7	1	12.4	2	2
S 8	1.2	14.3	1	1
S 9	1.2	13.5	1	1.5
S 10	1.2	14.3	1	2
S 11	1.2	14.3	2	1
S 12	1.2	13.6	2	1.5
S 13	1.2	13.9	2	2

3.5.3 Preparation of nitride sample for analysis

Specimen was sectioned after nitriding by wire-EDM to determine the microhardness and conducting the XRD analysis and wear test. Lower section of specimen is used to measure the cross-sectional micro hardness and middle one is used for XRD and wear testing of nitride sample.

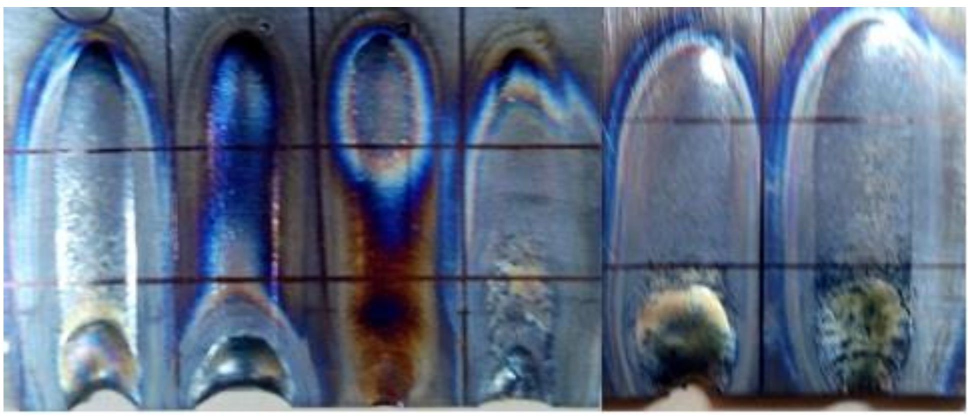


Figure 5 - Showing nitrided sample to be sectioned for hardness, XRD, and wear analysis

Hardness: Prior to the hardness measurement, specimen was polished with the help of sand paper of 220, 600, 1000, 1200 grade. Cross sectional area of nitride layer is used to measure the microhardness by Vickers Hardness testing machine.

XRD test: For XRD testing, nitride sample was cut in a dimension of 30 mm × 20 mm by wire cut EDM. Range of the diffraction angle is selected from 20^{o} to 90^{o}.

Wear test: Wear test was carried out on the same specimen as after XRD testing. The surface to be tested was cleaned using acetone prior to wear test. Rate of Wear was calculated by the loss of weight per unit time after wear testing in the following conditions.

Table 3 : Dry Wear test conditions

Parameter	Condition
Load (N)	30
Sliding Velocity (rpm)	328
Sliding distance (m)	30
Time (sec)	300
Track diameter (mm)	6

SEM: For the wear track analysis the sample obtained after wear testing was cut diametrically to the circular track by wire EDM of dimension 10 mm × 5 mm. Sectioned sample was thoroughly cleaned by acetone to remove the dust particles present on the surface of the wear track.

Chapter 4

Results and discussions

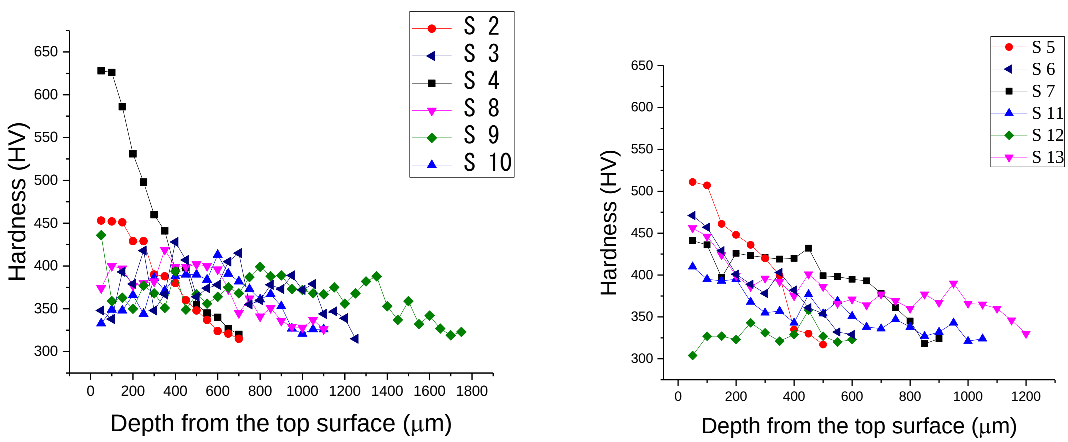
4.1 Micro-hardness of the Titanium nitride layer

Micro-hardness value of the nitrided layer was measured at the top surface as well as at the cross section by Vicker micro-hardness tester. The average micro-hardness value measured at the cross section was plotted against the applied current for different nitrogen gas pressure used during the TIG nitriding process are shown in Figure 7 (a, b). The maximum microhardness value of the titanium nitride layer reached up to 958 HV, which is three times higher than the substrate hardness value (320 HV). The decreasing trends of hardness value can be observed as we go in depth from the top surface due to simple mixture rule. Less amount of nitrogen is available at higher depth to form titanium nitrides or inter-metallic compound, however on increasing the Nitrogen pressure and energy density, higher hardening depth is observed on marginally sacrificing of maximum hardness because of a larger amount of nitrogen availability at the depth. Low maximum hardness at the top surface may be due to the cooling effect of nitrogen gas on the top surface because nitrogen is one of cooling gas and titanium has low thermal conductivity it accumulates the more heat on the inner side as compared to outer one. Nitrogen comes in direct contact with the top surface so cooling effect is observed. Figure 6 shows the typical distribution of hardness through the cross-sectional area.

4.1.1 Mechanics behind high hardness and hardening depth

Hardness of the nitride surface first increases by increasing nitrogen gas pressure but after a certain value (1.5 bar Nitrogen gas pressure) maximum hardness decreases. Excessive Nitrogen Pressure cool the melted zone on outer surface , because of rapid solidification less time was available to react titanium with nitrogen, ultimately less Titanium Nitrides was formed on the surface so that maximum hardness decreased but hardening depth increased by increasing energy density. Less nitrogen pressure leads towards low hardening depth because of less amount of nitrogen availability at the deeper side, However if optimum nitrogen gas pressure as (1.5 bar), and higher current density is used than maximum hardness and hardening depth both increased. Same thing can also be observed in Sample 3, sample 6, sample 9, and sample12. From Figure 6 (a, b) it is observed that the higher nitride depth layer is possible if the current is increased & Scan speed decreased, correspondingly energy density is increased. Figure 6 (a, b) shows the effect of pressure variation at two different current if scan speed remains constant.

Hardness value first increases from 1bar to 1.5 bar nitrogen gas pressure and then decreases with increases in nitrogen pressure. From the Figure, it is observed that the higher depth of the nitrided layer is possible if the current and pressure both are increased correspondingly energy density is increased. Several good results are obtained in accordance with higher hardness point of view are, 601 HV at (100 A current, 1.5 bar nitrogen gas pressure and 2.3 mm /s scan speed), 533 HV at (100 A current, 1.5 bar nitrogen gas pressure, and 3.5 mm /s scan speed), 631 HV at (120 A current, 1.5 bar nitrogen gas pressure and 2.3 mm /s scan speed), and 958 HV at (120 A current, 1.5 bar nitrogen gas pressure and 3.5 mm /s scan speed. At 1bar nitrogen gas pressure high hardness value is obtained as compared to the sample nitride at 2 bar nitrogen gas pressure on the cost of lower hardening depth.



(a) (b)

Figure 6 – Micro-hardness profile of the treated layers under different conditions across depth.

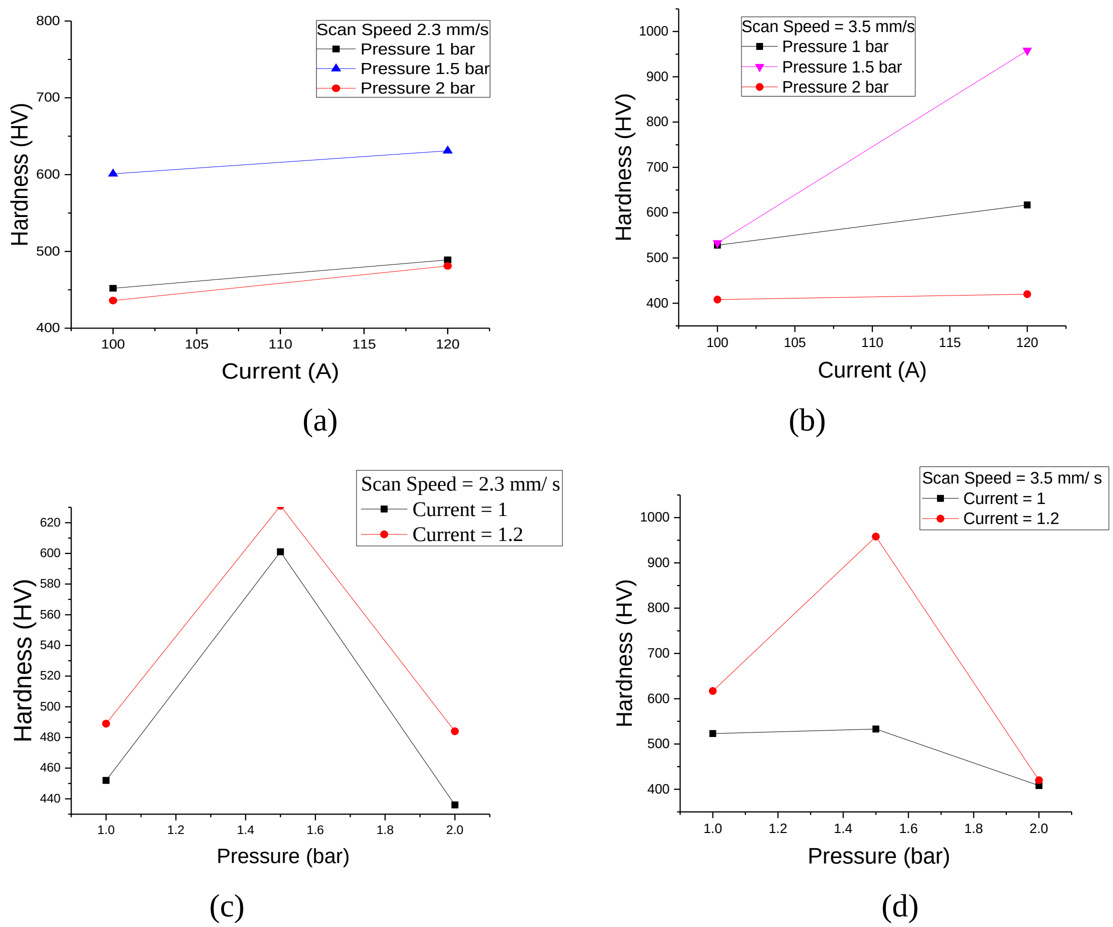
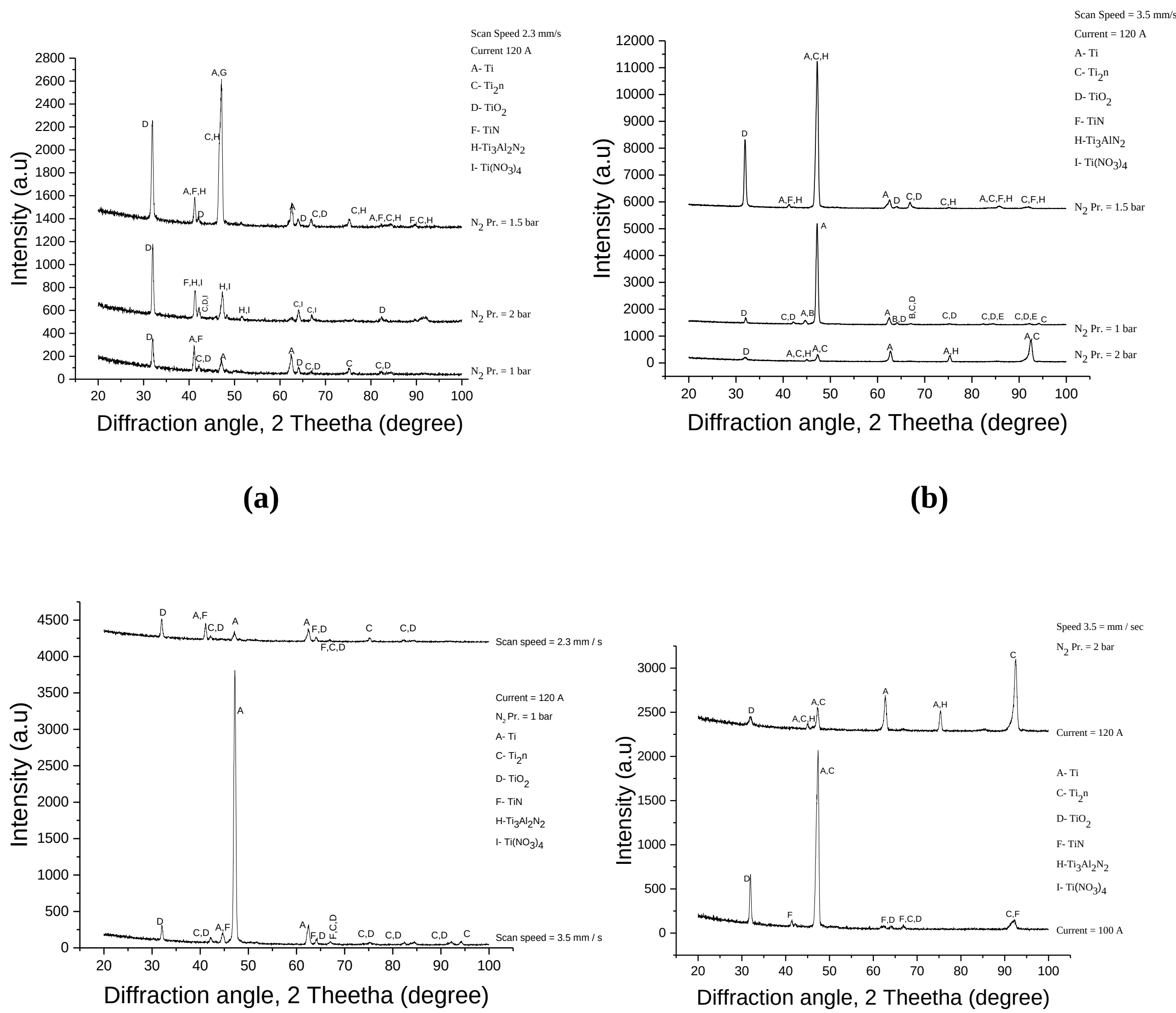


Figure 7 - Effect of current and pressure on surface Micro-hardness.

4.2 XRD Analysis of Titanium nitrided layers

XRD analysis was done on the Ti alloy surface after nitriding process to identify the compound present in the (Nitrogen + Heat) treated zone. The XRD spectra of the treated layer are performed at different condition are shown in Figure 8. In Figure 8 (a, b) it also observed that with increase in Nitrogen gas pressure intensity of titanium nitrides peak increases but after 1.5 bar nitrogen gas pressure up to 2 bar fall in intensity is observed. From the analysis of the plot, it is reaveled that TiN. Ti_2N, $Ti_xAl_yN_z$, and Ti_4N_{3-x} peaks are present on the nitrided surface. Which represent the reaction of nitrogen gas with the melted titanium alloy. A brief analysis of Figure 8(b), shows that intensity of Ti_2N and Ti_2AlN_2 peak is greater for the sample treated with 120 A current, 1.5 bar nitrogen gas pressure and scan speed value 3.5 mm/s, of intensity 5000 (a.u.), which indicate that larger proportion of titanium nitride and their intermetallic compound has formed. Along with these intermetallic compound peaks of Ti and TiO_2 are also observed. During melting of the substrate, nitrogen gas is supplied to the melted zone at the back of GTAW torch, from where nitrogen gas reacts with the melted Titanium alloy and form Titanium Nitrides and Intermetallic compounds.



(a) (b)

(c) (d)

Figure 8- XRD spectra of Ti-6Al-4V Nitrided sample prepared by TIG process under different condition.

4.3 Wear behaviour of Titanium nitrides layers

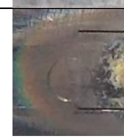
		Nitrogen gas pressure		
		1 bar	1.5 bar	2 bar
Current (A) and Scan speed mm/s	100 A 2.3 mm/s			
	100 A 3.5 mm/s			
	120 A 2.3 mm/s			
	120 A 3.5 mm/s			

Figure 9 – Worn out images of Ti-6Al-4V alloy after nitriding.

Wear behaviour of Ti-6Al-4V alloy and nitrided Ti-6Al-4V alloy was performed by ball on disc type rotating wear machine under dry condition. Images of the worn out sample at different process parameter are shown in Figure 9. Wear Rate was calculated by the loss of weight per unit time (g/min) after 5 minutes of test, the wear rate was plotted in Fig. 10.

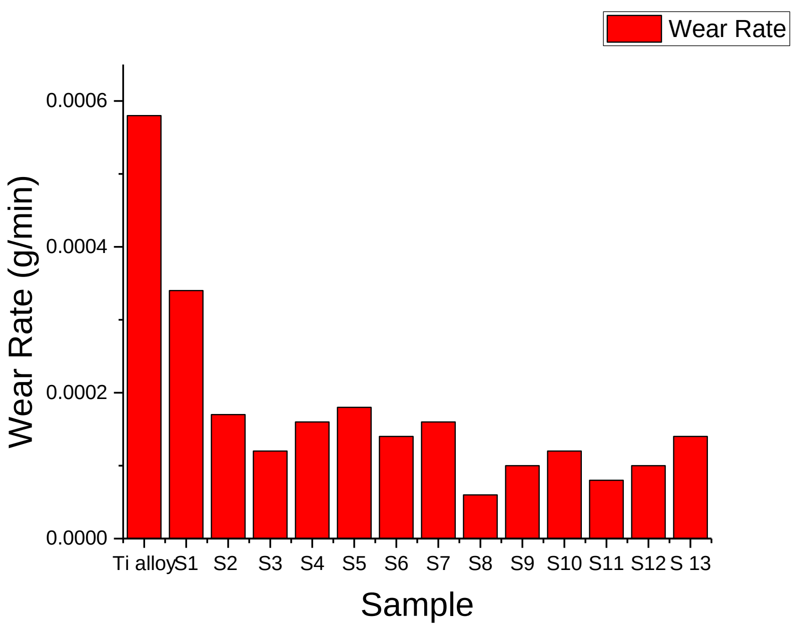


Figure 10 - Wear rate (g/min) of various specimen

The wear rate of the nitrided samples is in the range of 6×10^{-5}- 2.6×10^{-4} g/min which is almost 3 to 10 times less than as received substrate material (5.8×10^{-4} g/min). In Fig. 11 (a, b, c, d, e, f) effect of current , nitrogen gas pressure and scan speed on the wear rate can be observed.

4.3.1 Effect of Current

From Figure 11 (a, b), it is observed that wear rate decreases with the increase in current. It may because of the increase in energy density, a larger melted zone is created and more titanium reacts with nitrogen and form Titanium nitrides. Titanium nitrides provide high wear resistance, which resulted in low wear rate.

4.3.2 Effect of Nitrogen Pressure

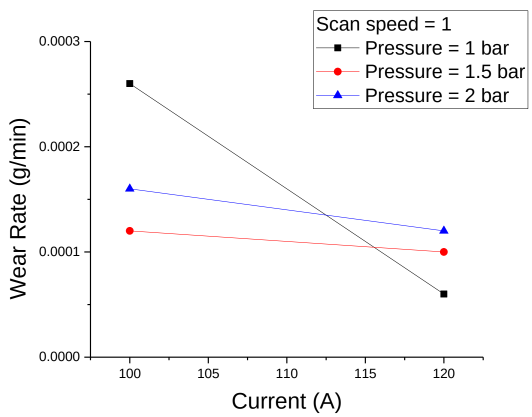
From Figure 11 (c) it is revealed that if optimum pressure of nitrogen gas is selected than weight loss can be reduced. If pressure is more or less than the optimum pressure value, wear has increased. This is because at high-pressure the surface is cooled rapidly and which results in less amount of melted titanium to react with nitrogen gas, this leads to less titanium nitride formation on the surface. While if low nitrogen gas pressure is provided in melted zone than nitrogen availability decreases to form titanium nitrides with Ti alloy consequently again less titanium nitrides have formed. Hence, in respect of high wear resistance optimum value of nitrogen gas pressure should be taken.

4.3.3 Effect of Scan Speed

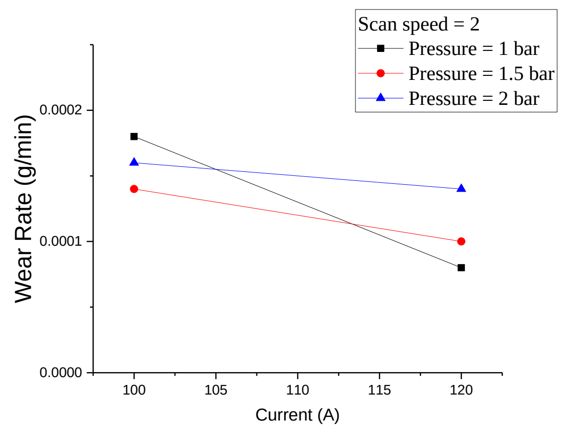
From Figure 11 (e, f) it is observed that, wear rate either increases or remains constant if scan speed increases when other nitriding parameters are constant except for the instance of 100 A current and 1 bar nitrogen gas pressure. With the increase in scan speed, energy density decreases, due to which depth of melted titanium alloy is less which results in less conversion of titanium into titanium nitrides. If scan speed increases from 2.3 mm/s to 3.5 mm/s, the wear rate suddenly increases. This may be due to low energy density, which results in low melting depth up to which nitride form.

While less wear rate is observed for low scan speed this may be because of higher energy density due to which titanium alloy was melted up to higher depth and more titanium nitrides were formed on the surface.

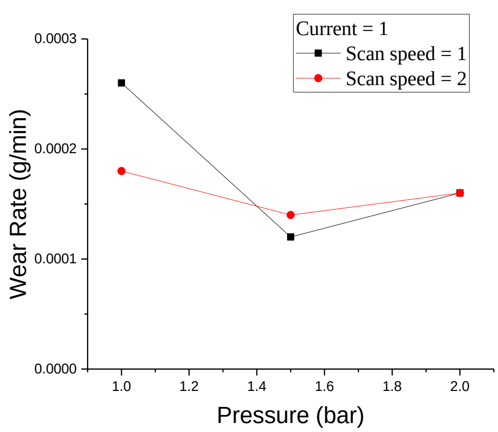
On the basis of wear analysis, it can be concluded that wear rate can be reduced if energy density increases which can be possible by two ways either increase in current or reduction in scan speed. However, if the amount of Nitrogen is increased up to certain limit it enhances the tribological properties due to enough amount of availability of nitrogen which results in improving the nitride forming tendency.



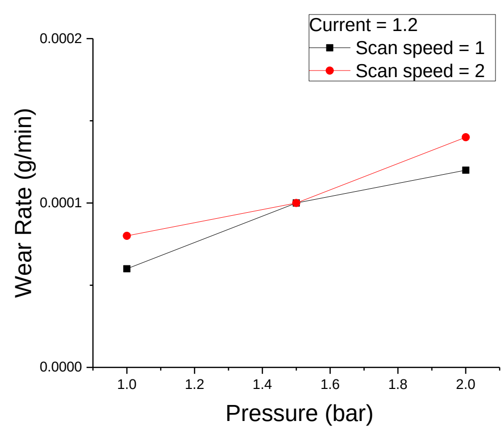
(a)



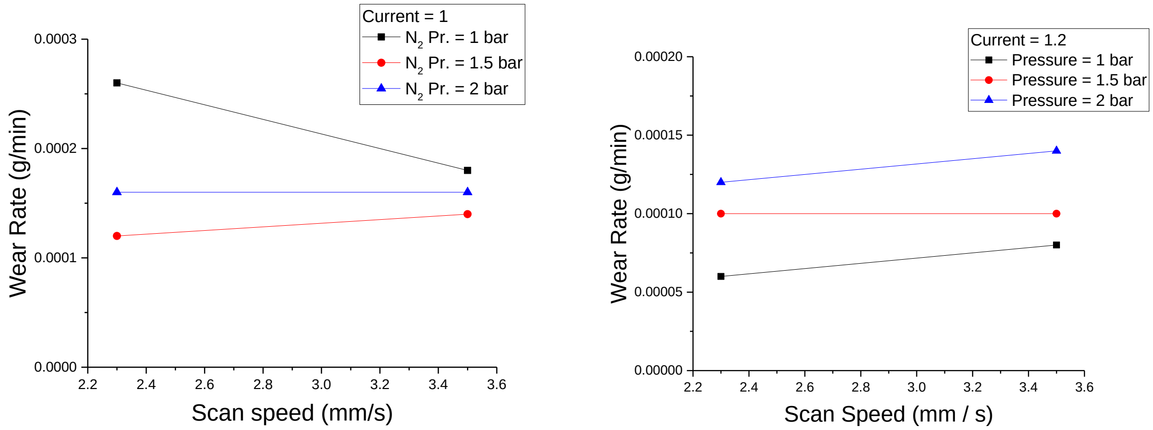
(b)



(c)



(d)

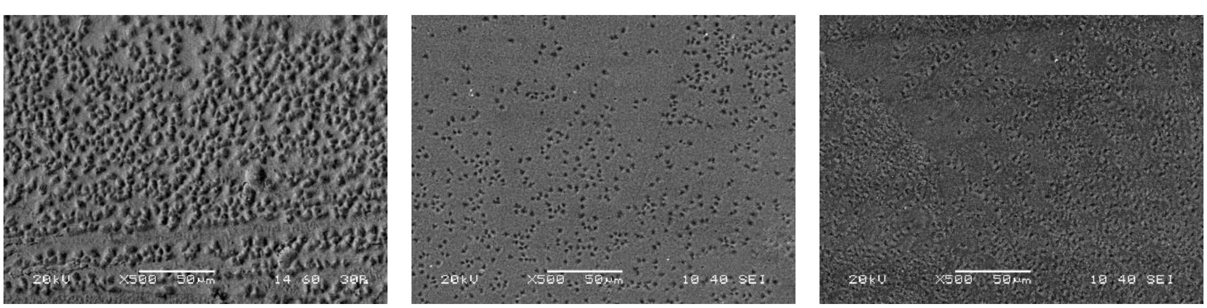


(e) **(f)**

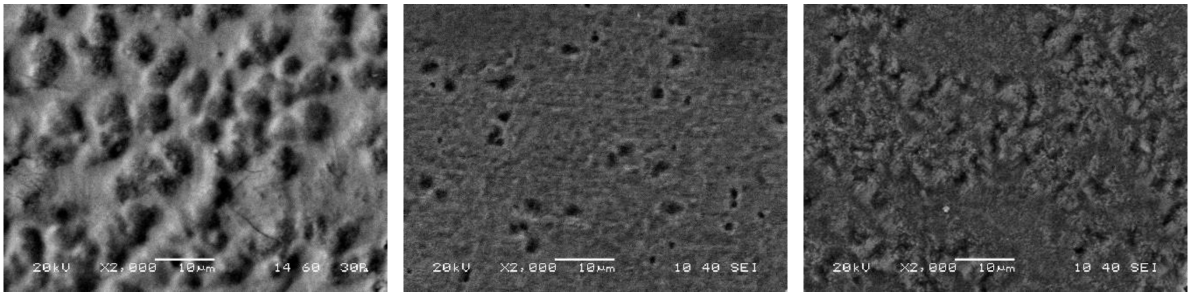
Figure 11 - Wear rate of nitrided specimen during ball-on-disc sliding wear test produced at different conditions.

4.4 Micro Structural analysis of nitride zone

Scanning electron microscopy (SEM) images of nitrided surface are studied for microstructure analysis. Images shown in Figure 12 (a, b, c,) and 12 (d, e, f) are taken at two different magnification scale at 500 X and 2000 X to visualize the micro structure of the nitride zone for different Nitrogen gas pressure. At the low nitrogen pressure (1 bar) coarse structure has found and on the surface, no pores are created because of low and uniform nitrogen gas pressure which results in very less wear. By increasing nitrogen pressure pores are created on the surface which can also be observed in Figure 12 (b, c and e, f). Nitrogen gas flowing at higher pressure act as a jet, when impinges on melted zone and creates porous cavity.



(a) Pressure 1 bar (b) Pressure 1.5 bar (c) Pressure 2 bar



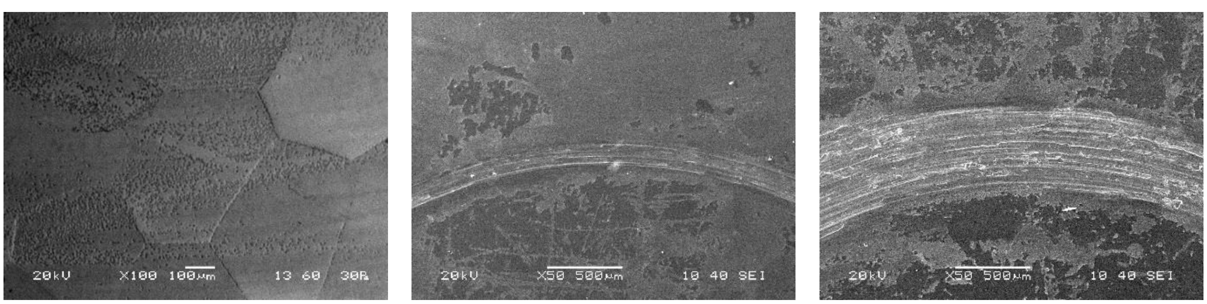
(d) Pressure 1 bar (e) Pressure 1.5 bar (f) Pressure 2 bar

Figure 12 - SEM Micrograph showing the dense array of TiN and micro structure at at current 120 A and scan speed 2.3 mm/s.

If nitrogen pressure is optimum as 1.5 bar, pores are less and fine structure has produced but at high nitrogen pressure more pores are produced and less finer structure has created.

SEM analysis of wear track

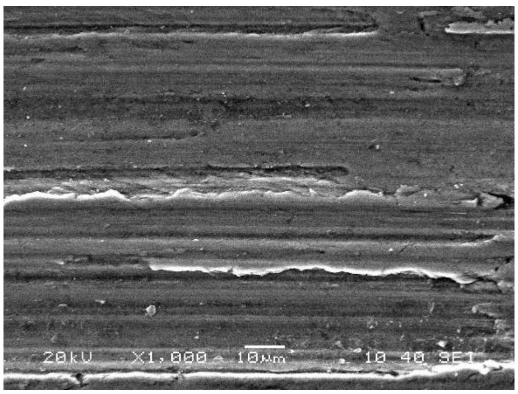
The worn out surface is found very rough with deep glowing grooves and spallation for the 1.5 bar nitrogen gas pressure and 2 bar as can be seen in Figure 14(a, b). For nitrogen gas pressure at 1 bar very less wear has occurred so it is not visible even at high magnification scale, same result is also found on the basis of wear rate for sample 8. However, significant wear has found with an increase in scan speed when other parameters are fixed.



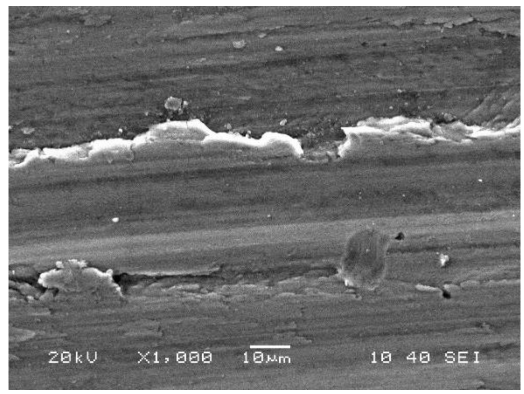
(a) Pressure 1 bar (b) Pressure 1.5 bar (c) Pressure 2 bar

Figure 13 - Worn surface morphologies of nitrided sample synthesized at current 120 A and scan speed 2.3 mm/s. The normal load in 30 N.

Plastic deformation is also observable on the worn out surface. The low adhesive wear resistance of Ti-6Al-4V alloy is attributed to its low hardness. Moreover, the high ductility and chemical activity of Ti-6Al-4V alloy lead to its strong tendency for adhesion. The transferred titanium associated with the adhesion becomes work-hardened after multiple contacts in the wear track, which in turn resulted in severe adhesive wear damage on the surface. This is confirmed by the deep grooves in Figure 14. Worn out surface of nitriding at 1 bar nitrogen gas pressure is found relatively smooth as compared to at 1.5 bar and 2 bar nitrogen gas pressure, as seen in Figure 13 at low magnification scale.



(a) Pressure 1.5 bar



(b) Pressure 2 bar

Figure 14 - Worn surface morphologies of nitrided sample at high magnification of current 120 A and scan speed 2.3 mm/s.

Chapter 5

Conclusion and future scope

Nitriding of Titanium alloy by using tungsten inert gas melting setup has successfully employed to form hard titanium aluminides, titanium nitrides and their intermetallic compounds on Ti-6Al-4V alloy. From the present research following conclusion were comes out:

1. Nitriding was performed by TIG melting method to produce Titanium nitrides, titanium aluminium nitride and their intermetallic compound on Ti-6Al-4V alloy by tungsten inert gas melting process in nitrogen environment.
2. Tungsten inert gas melting processed at operating current 120 A, scan speed 2.3 mm/s, and nitrogen gas pressure 1 bar produced pore and crack-free surface.
3. Pore and cracks are produced if nitrogen gas pressure increased as in 1.5 bar and 2 bar.
4. By selecting optimum nitrogen gas pressure and low scan speed depth of hardening layer increases. Maximum obtained hardening depth is 1.750 mm at 120 A current, 2.3 mm /sec scan speed and 1.5 bar nitrogen gas pressure.
5. Maximum surface hardness increases by increasing energy density and proper selection of nitrogen gas pressure.
6. Wear rate is found approximately one-tenth of the substrate for 120 A current, 2.3 mm/sec scan speed and 1 bar Nitrogen gas pressure. The improved resistance is due to the creation of hard protective layer of titanium nitrides.

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